Systematic Postsynthetic Modification of Nanoporous Organic Frameworks for Enhanced CO₂ Capture from Flue Gas and Landfill Gas

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Supporting Information

**ABSTRACT:** Controlled postsynthetic nitration of NPOF-1, a nanoporous organic framework constructed by nickel(0)-catalyzed Yamamoto coupling of 1,3,5-tris(4-bromophenyl)benzene, has been performed and is proven to be a promising route to introduce nitro groups and to convert mesopores to micropores without compromising surface area. Reduction of the nitro groups yields aniline-like amine-functionalized NPOF-1-NH₂ that has a micropore volume of 0.48 cm³ g⁻¹, which corresponds to 71% of the total pore volume and a Brunauer–Emmett–Teller surface area of 1535 m² g⁻¹. Adequate basicity of the amine functionalities leads to modest isosteric heats of adsorption for CO₂, which allow for high regenerability. The unique combination of high surface area, microporous structure, and amine-functionalized pore walls enables NPOF-1-NH₂ to have remarkable CO₂ working capacity values for removal from landfill gas and flue gas. The performance of NPOF-1-NH₂ in CO₂ removal ranks among the best by porous organic materials.

**INTRODUCTION**

Porous organic polymers (POPs), constructed from the assembly of organic building units, have gained significant attention as promising candidates for gas storage, separation, catalysis, and sensing because of their tunable functionality.¹,² The use of POPs for selective CO₂ capture from flue gas and landfill gas is very promising because of the stable covalent nature which keeps POPs intact under acidic and basic conditions in addition to the tolerance of these materials toward water.³,⁴ Exceptionally high surface area POPs like porous aromatic frameworks (PAFs) and porous polymer networks (PPNs) can be synthesized by performing homocoupling reactions of aryl building blocks, and the surface area of these materials can be further enhanced by controlling the reaction conditions.⁵,⁶ However, POPs composed of only carbon and hydrogen atoms do not perform well under gas separation settings at low pressure (1 bar) because of their lack of CO₂-philic sites which leads to low isosteric heats of adsorption for CO₂.¹⁰ It is well-documented that high surface area materials do not necessarily lead to high CO₂ uptake because gas uptake capacity depends on the favorable interactions between pore walls and guest gas molecules.¹¹ The physical and chemical stability of POPs allows for chemical modification, a process that can be used to impart desirable properties such as pore hydrophilicity, which is central for gas separation and storage applications.¹⁴

Among the new directions that have been explored to enhance sorbent–CO₂ interactions is pore functionalization using polar groups such as hydroxy, nitro, amine, sulfonate, azo, imidazole, triazine, imine, etc.⁵,¹⁰,¹³,¹⁵–²² Incorporation of these functionalities in the framework can be achieved by presynthesis modification of building blocks wherein CO₂-philic moieties are attached to building blocks before framework formation; self-functionalization where functional groups are formed as polymer networks grows, i.e., imidazole, azo, triazine; or through postsynthesis modification (PSM) processes in which functional groups are tethered to the pore walls after the framework assembly. Although presynthesis modification generally permits more controlled loading of functional groups, there are major drawbacks associated with the method. First, functionalization of building blocks often necessitates alternate reaction conditions (i.e., protection of functional groups), and these reactions are often time-consuming and nontrivial. Second, some reaction conditions require harsh conditions such as high temperature and acidic or basic media in which the
functional groups on the building blocks may not survive or which may lead to side reactions due to competition with other functional groups in the reaction media. Therefore, introducing target functionalities within the pores after framework formation (i.e., PSM) has been noted as an advantageous approach.

Recently, postnitration and subsequent reduction of porous networks has been demonstrated as a simple methodology for obtaining nitro- and amine-functionalized porous materials, respectively. However, this method leads to much lower surface areas due to uncontrolled loading of functional groups which block the ultramicropores, making them inaccessible to gas molecules. Partial framework collapse is also possible if the framework cannot tolerate prolonged exposure to harsh reaction conditions. We recently used PSM to functionalize NPOF-4 with −NO2 and −NH2 and investigated the effect on CO2 uptake and separation. Significant enhancement in CO2 binding affinity and selective binding over nitrogen and methane was observed. However, because of uncontrolled nitration the specific surface area of the −NO2 and −NH2 functionalized frameworks dropped dramatically and led to only modest CO2 uptake at low pressure. Thus, pore functionalization with CO2-phobic sites without compromising porosity remains a challenge for developing efficient CO2 adsorbents. Uncontrolled functional group loading often leads to functionalization of the ultramicropores which then become inaccessible to gas molecules. Therefore, new strategies for systematic functionalization of NPOFs are needed to retain the surface areas of these materials.

In this study, we designed a set of experiments to combine both high surface area and chemical functionality in NPOFs and to demonstrate the remarkable performance of functionalized NPOFs in CO2 separation from flue gas and landfill gas. NPOF-1 under controlled conditions afforded NPOF-1-NO2 and NPOF-1-NH2, which retain high surface area and accessible micropores. We also show that prolonged functionalization reaction time and the use of excess amounts of nitric acid have detrimental impact on the textural properties of the functionalized frameworks which diminish their use as CO2 adsorbents. For simplicity, the nitrated NPOF-1, made by using 2 equiv of HNO3 and the reduced amine-functionalized derivative will be denoted as NPOF-1-NO2 and NPOF-1-NH2, respectively. While NPOFs nitrated using excess amounts of nitric acid and the reduced amine-functionalized derivatives will be denoted as NPOF-1-NO2(xs) and NPOF-1-NH2(xs), respectively.

EXPERIMENTAL SECTION

General Techniques, Materials, and Methods. All starting materials and solvents, unless otherwise noted, were obtained from Acros Organics and used without further purification. 1,3,5-tris-(4-bromophenyl)benzene (TPBB) was synthesized according to the literature. Solvents were dried by distillation. Air-sensitive samples and reactions were handled under an inert atmosphere of nitrogen using either glovebox or Schlenk line techniques. Elemental microanalyses were performed at the Midwest Microlab, LLC. Liquid 1H and 13C NMR spectra were obtained on a Varian Mercury-300 MHz NMR spectrometer (75 MHz carbon frequency). Solid-state 13C cross-polarization magic angle spinning (CP-MAS) NMR spectra for solid samples were taken at Spectral Data Services, Inc. Spectra were obtained using a Tecmag-based NMR spectrometer operating at a H-1 frequency of 363 MHz, using a contact time of 1 ms and a delay of three seconds for CP-MAS experiments. All samples were spun at 7.0 kHz. Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q-5000IR series thermal gravimetric analyzer with samples held in 50 μL platinum pans under an atmosphere of air (heating rate 5 °C/min). For scanning electron microscopy imaging (SEM), samples were prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The samples were then coated with platinum at a pressure of 1 × 10−5 mbar under a nitrogen atmosphere for 70 s before imaging. Images were taken on a Hitachi SU-70 scanning electron microscope. Powder X-ray diffraction data were collected on a Panalytical X’pert pro multipurpose diffractometer. Samples were mounted on a sample holder and measured using Cu Kα radiation with a 2θ range of 1.5–35. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet-Nexus 670 spectrometer furnished with an attenuated total reflectance accessory. Porosity and gas sorption experiments were performed using a Quantachrome Autosorb iQ volumetric analyzer using adsorbates of UHP grade. In a typical experiment, a sample of polymer (~50 mg) was loaded into a 9 mm large bulb cell (Quantachrome) of known weight which is then hooked up to the gas analyzer and degassed at 130 °C/1.0 × 10−5 bar for 12 h. The degassed sample was refilled with helium, weighed precisely, then transferred back to the analyzer. The temperatures for adsorption-controlled measurements were controlled by using a refrigerated bath of liquid nitrogen (77 K) and a temperature-controlled water bath (273 and 298 K).

Synthesis of NPOF-1. NPOF-1 was synthesized following a modified method from previous reports. A 200 mL reaction flask equipped with a stir bar was charged with TPBB (400 mg, 0.736 mmol) then filled with N2 after evacuation under vacuum. Under inert conditions (glovebox), Ni(COD)2 (1.03 g, 3.75 mmol), COD (0.4 mL, 3.75 mmol), 2,2-bipyridyl (585 mg, 3.75 mmol), 60 mL of anhydrous DMF, and 40 mL of freshly distilled THF were added. The resultant suspension was heated at 80 °C for 24 h. The mixture was cooled to room temperature, and 40 mL of 6 M HCl was added; the mixture was then stirred for 3 h. The resultant white powder was filtered and washed with 2 M HCl, hot water, THF, ethanol, and acetone and dried under reduced pressure to afford NPOF-1 as a white powder (255 mg, 87% yield) Anal. Calcd for C24H18N2O2: C, 71.86%; H, 3.70%; N, 4.70%. Synthesis of NPOF-1-NO2. A 50 mL round-bottom flask was charged with 10 mL of concentrated H2SO4 then cooled to 0 °C. To this solution, 100 mg of NPOF-1 was added in small portions followed by dropwise addition of 93 μL fuming HNO3; the mixture was stirred for 90 min at 0 °C. The mixture was poured into 75 mL of ice and stirred for 30 min at room temperature. The resulting powder was isolated by filtration through a medium glass frit and washed with copious amounts of water and ethanol and dried under reduced pressure to afford NPOF-1-NO2 (108 mg) as a brownish powder. Anal. Calcd for C24H18N2O2: C, 65.76%; H, 2.76%; N, 9.59%. Found: C, 71.86%; H, 3.70%; N, 4.70%.

Synthesis of NPOF-1-NH2. A 50 mL round-bottom flask equipped with a stir bar was charged with 80 mg of NPOF-1-NO2, 10 mL of methanol, and 10 mL of distilled water under nitrogen. The resultant suspension was degassed with N2 for 20 min before sodium dithionite (1.2 g, 6.9 mmol) was added; then the mixture was heated to 75 °C for 18 h. The resultant material was filtered and suspended in warm water (25 mL) for
30 min. The suspension was filtered and washed with warm water twice. The resultant polymer was suspended in 25 mL of 4 M HCl to ensure complete reduction to amine then was washed with water followed by 2 M NaOH to neutralize the amine. The isolated product was suspended in warm water (30 mL) for 60 min. After filtration, the polymer was suspended in warm ethanol and THF twice for 30 min cycles. The polymer finally was filtered and washed with methanol and dried overnight under vacuum at 120 °C to yield dark brownish NPOF-1-NH\(_2\) (68 mg). Anal. Calcld for C\(_{24}\)H\(_{18}\)N\(_3\): C, 82.73%; H, 5.21%; N, 12.06%. Found: C, 75.47%; H, 4.22%; N, 5.01%.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** Synthesis of NPOF-1 was carried out according to literature methods as presented in Scheme 1.

We have noticed that room-temperature polymerization procedures resulted in low surface area materials; therefore, heating the reaction mixture to 80 °C was needed to optimize the porosity of NPOF-1.\(^2^9\) Additionally, using a mixture of DMF/THF solvent system and heating all reactants and reagents together to 80 °C starting from room temperature resulted in a slight increase in the reported surface area (1950 vs 2060 m\(^2\) g\(^{-1}\)).\(^2^7\) The nitration of NPOF-1 was performed at 0 °C in the presence of 2 equiv of HNO\(_3\) per phenyl ring for 90 min resulting in NPOF-1-NO\(_2\). NPOF-1 was also nitrated with excess HNO\(_3\) for 6 h at 0 °C (previously published method) and named as NPOF-1-NO\(_2\)(xs).\(^1^0\) However, the long nitration period and use of excess HNO\(_3\) results in much lower surface area for NPOF-1-NO\(_2\)(xs) (749 m\(^2\) g\(^{-1}\)) compared to NPOF-1-NO\(_2\) (1295 m\(^2\) g\(^{-1}\)). The sorption data was collected for both nitro-functionalized materials to reveal the effect of over-functionalization. Functionalized NPOFs were then reduced to afford corresponding amine-functionalized frameworks, namely, NPOF-1-NH\(_2\) and NPOF-1-NH\(_2\)(xs). Figure 1 shows the FT-IR spectra of the pristine polymer NPOF-1 and its postsynthetic functionalized derivatives. Upon nitration, new FT-IR bands appeared at 1532 and 1350 cm\(^{-1}\), which can be ascribed to the asymmetrical and symmetrical stretching of NO\(_2\), respectively.\(^2^6\) Reduction of nitro groups to amino functionalities resulted in the disappearance of these bands and the presence of new bands at 3350 and 3230 cm\(^{-1}\) that correspond to asymmetrical and symmetrical N–H stretching, respectively. According to powder X-ray diffraction studies, all frameworks are amorphous and lack long-range ordering (Figure S3). SEM images revealed aggregated spherical particles of variable sizes, as shown in Figure S4. TGA analysis (Figure S1) shows that the functionalized polymers lost only ∼5 wt % up to 300 °C after subtracting the initial weight lost, which is due to residual solvents and/or moisture. To gain more information about the chemical composition of the polymers, we performed elemental analysis, which can be used to estimate nitrogen loading. Interestingly, the use of excess HNO\(_3\) resulted in a lower than expected nitration levels of 1,4 substituted phenyl rings (∼0.59 nitro/phenyl ring) while controlled nitration yields ∼0.4 nitro loading per phenyl ring, which is still more efficient than previously reported methods for POPs resulting in ∼0.25–0.3 N/phenyl.\(^1^4\) Presumably, the
NPOFs show a sharp uptake at the very low pressure region depicted in Figure 2. All nitrogen isotherms of functionalized POPs are characterized by means of CO2 (273 K) and N2 (77 K) adsorption measurements for ultramicro and micro/mesoporous materials instead of N2 adsorption at 77 K (centered around 42.5 Å) were successfully converted to micropores (<4 Å). It was expected to observe a slight shift in the pore width maxima after reduction of NO2 to NH2 groups due to size difference; however, this change was almost negligible. The use of CO2 adsorption at 273 K has been often employed to calculate ultramicroporosity (pores less than 0.7 nm) for microporous materials instead of N2 adsorption at 77 K which is consistent with their expected microporous nature. In contrast, NPOF-1 displayed a gradual increase in N2 uptake and pronounced hysteresis at P/P0 > 0.1 as a result of mesopores and framework swelling. The textural properties of all frameworks are listed in Table 1. As stated earlier, NPOF-1 was synthesized according to a modified published procedure and exhibits high surface area (SA_determined by NLDFT cm3 g−1). The combination of high surface area and chemical functionality is crucial for improving CO2 uptake. Subsequent reduction of nitro-functionalized NPOFs yielded NPOF-1-NH2 and NPOF-1-NH2(xs) with surface areas of 1535 and 1074 m2 g−1, respectively. Pore size distribution was estimated by fitting the nitrogen uptake branch of the isotherms using the nonlocal density functional theory (NLDFT) (cylindrical/spherical pore geometry with zeolites/silica) model and was found to be in a broad range of micropore/mesopore region for NPOF-1. After the nitration of NPOF-1, all of the mesopores (centered around 42.5 Å) were successfully converted to micropores (9–13 Å). It was expected to observe a slight shift in the pore width maxima after reduction of NO2 to NH2 groups due to size difference; however, this change was almost negligible. The use of CO2 adsorption at 273 K has been often employed to calculate ultramicroporosity (pores less than 0.7 nm) for microporous materials instead of N2 adsorption at 77 K. This is due to the much slower diffusion of N2 at 77 K which could prevent N2 adsorption in ultramicropores and lead to very long data collection time. Therefore, we have also employed CO2 as a probe molecule to obtain more information about pore sizes, and this revealed that ultramicropores (<4 Å) were created after postsynthetic-modification of NPOF-1 (Figure S5). Pore volumes of NPOF-1 and its derivatives are calculated from N2 isotherms collected at 77 K using NLDFT under the same settings used for PSD calculation. Because the scope of the current study is to maintain and/or generate nitrogen content increases upon reduction (5.01%) due to replacement of oxygen with a much lighter atom, hydrogen. It is worth noting that the deviation in elemental analysis results is common with amorphous polymers, especially for postfunctionalized POPs. This could be a result of one or a combination of several factors such as (1) frameworks are considered to be nondefective structure; (2) remaining/unreacted end groups; (3) inaccessible pores where functionalization does not take place; and (4) trapped salts, reagents, and catalysts inside the pores.30−32

Textural Properties. The specific surface area and pore size distribution of NPOF-1 and its derivatives were comparatively characterized by means of CO2 (273 K) and N2 (77 K) sorption–desorption measurements for ultramicro and micro/mesopores, respectively. The corresponding nitrogen adsorption isotherms and pore size distribution of NPOFs are depicted in Figure 2. All nitrogen isotherms of functionalized NPOFs show a sharp uptake at the very low pressure region (P/P0 < 0.01) and then form a plateau in most of the pressure range, which is consistent with their expected microporous nature. In contrast, NPOF-1 is consistent with their expected microporous nature. In contrast, NPOF-1 was synthesized according to a modified published procedure and exhibits high surface area (SA_BET = 2062 m2 g−1). As expected, the surface areas of all functionalized polymers are lower compared to NPOF-1. The use of excess (125 equiv/phenyl) HNO3 and longer reaction time (6 h), NPOF-1-NO2(xs) shows the lowest surface area (749 m2 g−1).

![Figure 2. Nitrogen isotherms at 77 K (A) and pore size distribution from NLDFT using N2 at 77 K (B).](Image 96x580 to 528x749)

Table 1. CO2 Uptakes at 298 K, Q0, and IAST Selectivity Results

<table>
<thead>
<tr>
<th>polymer</th>
<th>SA_BET</th>
<th>V_Mic,DFT</th>
<th>0.15 bar</th>
<th>1 bar</th>
<th>Qe</th>
<th>CO2/N2</th>
<th>CO2/CH4</th>
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<tr>
<td>NPOF-1</td>
<td>2062</td>
<td>0.28 (19)</td>
<td>11 (1)</td>
<td>67 (1)</td>
<td>21.7</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>NPOF-1-NO2</td>
<td>1295</td>
<td>0.36 (58)</td>
<td>27 (2.5)</td>
<td>111 (1.7)</td>
<td>29.2</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>NPOF-1-NO2(xs)</td>
<td>749</td>
<td>0.23 (70)</td>
<td>26 (2.4)</td>
<td>88 (1.3)</td>
<td>32.0</td>
<td>45</td>
<td>11</td>
</tr>
<tr>
<td>NPOF-1-NH2</td>
<td>1535</td>
<td>0.48 (71)</td>
<td>47 (4.3)</td>
<td>166 (2.5)</td>
<td>32.1</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>NPOF-1-NH2(xs)</td>
<td>1074</td>
<td>0.35 (77)</td>
<td>39 (3.5)</td>
<td>129 (1.9)</td>
<td>32.6</td>
<td>41</td>
<td>8</td>
</tr>
</tbody>
</table>

“Brunauer–Emmett–Teller (BET) surface areas are reported in m2 g−1. Micro pore volume determined by NLDFT cm3 g−1; the values in parentheses are the percentage of micropore volume relative to total pore volume. The uptakes of CO2 at corresponding pressure in mg g−1 at 298 K; the values in parentheses are the ratio of the uptake to NPOF-1 in the same column to illustrate the enhancement in uptake compared to NPOF-1. Isosteric heat of adsorption (in kJ mol−1) of corresponding gas at zero coverage calculated from isotherms collected at 273 and 298 K using the virial equation. Selectivity calculated by IAST at 298 K and 1 bar.
microporosity in the frameworks, we have calculated micropore percentage rather than reporting total pore volume from a single point calculation. Micropore and total pore volumes are calculated by considering the pores up to 2 and 10 nm, respectively. For total pore volume calculation, 10 nm thresholds were selected because PSD analysis did not show any pores beyond 10 nm. As shown in Table 1, micropore volume percentage increased dramatically up to 77% of total pore volume for NPOF-1-NH2(xs). Moreover, a closer look at the data reveals that NPOF-1-NH2 might be more beneficial for CO2 capture because it possesses 0.48 cm² g⁻¹ micropore volume which corresponds to 71% of its total pore volume and is 37% higher compared to that of NPOF-1-NH2(xs). This new synthetic strategy enables controlled functional group loading while maintaining high porosity, making the functionalized networks very promising for selective CO2 capture from gas mixtures as detailed below.

**Gas Uptake and Selectivity Studies.** To assess the potential of functionalized NPOFs in CO2 capture from flue gas and landfill gas, adsorption isotherms on activated samples for carbon dioxide, methane, and nitrogen were collected at 273 and 298 K. All isotherms are fully reversible, illustrating the facile uptake and release of gases, which makes them energetically attractive for gas separation applications. It is well-documented that microporosity is essential for CO2 capture from gas mixtures that possess low CO2 content. We have recently shown that high percentage of microporosity in the frameworks, 35 functionalized CMPs, 36 ALPs, 18, 37 BILPs, 5, 40, 41 metal-containing organic polymers, 42, 43 and amine-appended POPs.

Comparison of methane uptake reveals that in contrast to CO2 functionalization with polar groups does not enhance methane uptake as a result of the low CH4-framework interactions (∼22 kJ mol⁻¹). These findings suggest that pore functionality along with microporosity are central parameters for enhanced CO2 uptake at low pressures (up to 1 bar) while high accessible surface area improves CH4 uptake.

Low-pressure gas sorption measurements for CO2 and CH4 were also used in order to calculate the enthalpies of adsorption (Qₑ) using the virial method. The virial equation is fitted to isotherms collected at 273 and 298 K. The Qₑ values and CO2 uptakes for NPOFs are summarized in Table 1. The Qₑ values show all functionalized NPOFs to have higher heats of adsorption for CO2 over nonfunctionalized NPOF-1 over the entire loading range. The enhanced Qₑ values are expected because of both chemical and physical pore modification. In addition to the electronic nature of −NH2 and −NO2, upon framework functionalization, the pore size of NPOF-1 is also reduced, and this provides higher adsorption potentials for CO2 via possible multipore wall interactions. Pore modification increases CO2 binding affinity from 21.7 kJ mol⁻¹ to 32.6 kJ mol⁻¹ for NPOF-1-NH2. These observations again can be ascribed to the polarizable nature of the CO2 molecule and its large quadrupole moment in addition to Lewis acid-base interactions between CO2 and primary amines. The Qₑ drops with higher CO2 loadings for functionalized NPOFs as functional sites become saturated; however, nonfunctionalized NPOF-1 did not follow this trend because of lack of chemical heterogeneity. It is worth mentioning that the interaction between aniline-like primary amines and CO2 resulted in a moderate Qₑ value which is desired for cost-effective CO2 adsorbents. On the other hand, alkyl amine-appended MOFs 48 and POPs 5, 40, 41 resulted in much higher (>50 kJ mol⁻¹) binding affinities which require higher energy input for regeneration of the adsorbents. The high binding affinity of alkylamines toward CO2 originates from high electron density localized on nitrogen.

![Image](https://example.com/image.png)

**Figure 3.** CO2 uptakes at 273 (A) and 298 K (B) and corresponding Qₑ plot (C) of NPOFs.

DOI: 10.1021/acs.jpcc.5b12247

J. Phys. Chem. C XXX, XXX, XXX–XXX
sites in addition to multiple amine (inter and/or intra molecular)–CO$_2$ interactions favored by the flexible nature of the tethered amines. On the other hand, the electron densities of aniline-like amines are delocalized through the $\pi$-electrons of benzene rings directly linked to the amine. In this case, the amine basicity is much lower; therefore, only physical interactions between the amine sites and CO$_2$ molecules take place. Nevertheless, the $Q_a$ values for functionalized NPOFs are strong enough to accommodate high CO$_2$ at low pressures and exceed most of the best performing materials such as BILPs$^{8}$ and bio-MOF-11.$^{49}$

Selectivity of an adsorbent toward CO$_2$ is also as important as the uptake because CO$_2$ is not the main component in the gas mixtures to be purified. Therefore, great efforts have been directed toward the design of porous materials that have high CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivity for CO$_2$ removal from flue gas and landfill gas, respectively. Ideal adsorbed solution theory (IAST) is a widely accepted method for investigating the selectivity of porous adsorbents using only pure gas isotherms to calculate gas mixture adsorption.$^{50}$ As depicted in Figure 4, the IAST results indicate that NPOF-1-NO$_2$(xs) has the highest selectivity among the NPOFs studied here for CO$_2$/N$_2$ as it has the lowest surface area and therefore lowest N$_2$ uptake at 298 K. NPOF-1-NH$_2$ has a CO$_2$/N$_2$ selectivity of 25 at 298 K and 1 bar. However, for CO$_2$/CH$_4$ selectivity, NPOF-1-NH$_2$ performed very similarly to NPOF-1-NO$_2$(xs) because of much higher CO$_2$ uptake of the former at 0.5 bar. The high surface area along with amine functionality allows NPOF-1-NH$_2$ to perform better at higher CO$_2$ concentrations.

**Working Capacity Study.** Although numerous porous organic and organic–inorganic hybrid materials have been evaluated for CO$_2$ capture and separation, a careful analysis of the trade-off between selectivity and uptake capacity was not evaluated until recently.$^9$ The general observation made by Bae and Snurr was that high surface area favors CO$_2$ separation from landfill gas in pressure swing adsorption (PSA), whereas narrow pore size and high enthalpies of adsorption lead to optimal CO$_2$ removal from flue gas using vacuum swing adsorption (VSA). Furthermore, five evaluation criteria (vide infra) were adopted from the chemical engineering field to investigate the effectiveness of porous adsorbents: CO$_2$ uptake, working capacity for CO$_2$, adsorbent regenerability, selectivity under adsorption conditions, and sorbent selection parameter. These criteria, although not perfect, provide a comprehensive approach for assessing the suitability of porous adsorbents in CCS processes.

Because 87% of the world’s total energy production comes from burning fossil fuels, there is an urgent need for selective capture of CO$_2$ from flue gas. A careful analysis of the performance of NPOFs for this task (CO$_2$/N$_2$: 10/90) using VSA at 298 K is presented in Table 2. The working capacities ($\Delta N$) were determined by calculating the CO$_2$ adsorption difference between 1.0 and 0.1 bar using IAST-derived uptakes. According to Table 2, NPOF-1-NH$_2$ showed great CO$_2$ uptake enhancement at low pressures (4.3 fold higher compared to NPOF-1) due to the unique combination of high micropore volume and chemical functionality in addition to optimum isosteric heats of adsorption for CO$_2$; as a consequence, NPOF-1-NH$_2$ revealed the highest working capacity (0.66 kg mol$^{-1}$) compared to other NPOFs evaluated here. On the other hand, the lower micropore volume and surface area of NPOF-1-NH$_2$(xs) resulted in ~17% less working capacity, although both materials have primary amine-functionalized frameworks and very similar $Q_a$ for CO$_2$. It is worth noting that the high surface area of NPOF-1-NH$_2$ and low partial pressure (10%) of CO$_2$ resulted in low CO$_2$/N$_2$ selectivity and therefore low S value compared to NPOF-1-NH$_2$(xs), with the latter displaying much lower working capacity.

Switching from coal-fired power plants to natural gas-fired power plants presents an alternative strategy to mitigate CO$_2$ emissions before renewable energy sources become widely available because natural gas has a lower carbon footprint. For the same reason, the use of natural gas in automotive applications is highly desired; however, natural gas found in reservoirs has tangible amounts of CO$_2$, N$_2$, and H$_2$S that need

![Figure 4. Selectivity calculated by IAST for CO$_2$/N$_2$ (A) and CO$_2$/CH$_4$ (B) at 298 K.](image-url)
to be minimized before transport and use.\textsuperscript{51} Natural gas as well as landfill gas purification processes involve CO\textsubscript{2} removal to prevent pipeline corrosion and to increase the energy density of this methane-rich gas making onboard storage and use more efficient. Therefore, we assessed NPOFs performance in landfill gas purification from CO\textsubscript{2} under VSA conditions at 298 K (Table 3). NPOF-1-NH\textsubscript{2} outperformed all other NPOFs

<table>
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<th>adsorbent</th>
<th>$N_{1}^{ads}$</th>
<th>$\Delta N_{1}$</th>
<th>% R</th>
<th>$a_{12}^{ads}$</th>
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<tr>
<td>TBILP-2\textsuperscript{13}</td>
<td>2.20</td>
<td>1.84</td>
<td>83.7</td>
<td>7.6</td>
<td>63</td>
</tr>
<tr>
<td>BILP-1\textsuperscript{2}</td>
<td>2.01</td>
<td>1.71</td>
<td>85.3</td>
<td>6.0</td>
<td>34</td>
</tr>
<tr>
<td>SNU-C-Cl\textsuperscript{11}</td>
<td>1.51</td>
<td>1.21</td>
<td>80.6</td>
<td>9.7</td>
<td>84</td>
</tr>
<tr>
<td>dimide-POP\textsuperscript{23}</td>
<td>1.39</td>
<td>1.05</td>
<td>76.0</td>
<td>5.8</td>
<td>16</td>
</tr>
</tbody>
</table>

reported in Table 3 in terms of working capacity (2.10 kg mol\textsuperscript{-1}). Because the concentration (partial pressure) of CO\textsubscript{2} is higher in landfill gas (50%), the outcome of high surface area adsorbents along with chemical functionality becomes more pronounced. For instance, NPOF-1-NH\textsubscript{2} gives a $\sim$20% enhancement in working capacity compared to NPOF-1-NH\textsubscript{2}(xs) in the case of flue gas; however, this difference becomes $\sim$27% in the case of landfill gas separation due to higher partial pressure of CO\textsubscript{2}. Although the high CO\textsubscript{2}/CH\textsubscript{4} selectivity of NPOF-1-N\textsubscript{2}(xs) due to low surface area results in a higher $S$ parameter, the much lower working capacity compared to NPOF-1-NH\textsubscript{2} makes it a less promising candidate for CO\textsubscript{2} separation from landfill gas. On the other hand, the ideal combination of high surface area, binding affinity, and microporous nature of NPOF-1-NH\textsubscript{2} gives rise to high CO\textsubscript{2}/CH\textsubscript{4} selectivity and working capacity, which results in a very high $S$ value. This suggests that NPOF-1-NH\textsubscript{2} can be more suitable for CO\textsubscript{2} separation from mixtures where CO\textsubscript{2} concentration is at or above 50%.

## CONCLUSION

We have synthesized NPOF-1 and presented its postsynthetic modification of the material to functionalize the framework with −NO\textsubscript{2} and −NH\textsubscript{2} functionalities. Using stoichiometric amounts of nitric acid and shortening the reaction time allowed us to maintain and/or generate ultramicropores and to incorporate polar functional groups, which are essential properties for CO\textsubscript{2} capture at low pressures ($<1$ bar). We have shown that coupling the high surface area and aniline-like amine functionality in NPOF-1-NH\textsubscript{2} yields very high CO\textsubscript{2} working capacity and selectivity, which result in a high sorbent selection parameter for CO\textsubscript{2} capture from landfill gas under VSA settings.

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b12247.

Additional experimental details; TGA, XRD, and SEM data; fitting data for BET; and selectivity calculations. (PDF)

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### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award DE-SC0002576. T.I. thanks the Ministry of National Education of Turkey for graduate fellowship.

### REFERENCES


(28) Calculated elemental analysis values are based on 1 nitro and 1 amine per phenyl ring for NPOF-1-NO2 and NPOF-1-NH2, respectively.


